Effect of ion and electron beam irradiation on surface morphology and optical properties of PVA

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Polyvinyl alcohol (PVA) is a well-known friendly polymer for paper-making, textiles, and a variety of coatings, biomedical applications such as artificial pancreas, synthetic vitreous body, wound dressing, artificial skin, and cardiovascular device. In this paper, ion/electron beam is employed to get insight into the irradiation effect on surface morphology and optical properties of PVA polymer. UV-Vis spectra are recorded to investigate the effect of induced defects on the optical band gap and the formed carbon clusters size. Scanning electron microscopy (SEM) is used to relate and investigate surface morphology and optical properties of the target polymer with different doses (15, 30 and 60 min). Also, PVA polymer is subjected to theoretical studies by using semi-empirical PM7 quantum chemical method.

Keywords: Electron/ion beams, Optical band gap, Polyvinyl alcohol (PVA), UV-Vis spectra

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I. INTRODUCTION

Polymers have been in rapid development during the last few decades because of their low cost, easy processability, low weight, high quality surfaces and easy fabrication of thick and thin samples, etc. [1]. The most applicable interest in polymers appears from their special physico-chemical properties, such as ion transport, electrochemical effects, photo activity, catalytic agents and electronic junction effects. Ion/electron beam bombardment of a solid target causes a significant transformation to the structure and properties of the bombarded surface [2, 3]. When a beam of energetic particles enters a solid, several processes are initiated in the area of interaction [4]. A fraction of the particles are backscattered from the surface layers, while the others are slowed down in the bulk. The collision induces secondary processes such as recoil and sputtering of constituent atoms, defect formation, electron excitation and emission, and photon emission. Thermal and radiation-induced diffusion contributes to various phenomena of mixing of constituent elements, phase transformation, amorphization, crystallization, track formation, permanent damage, and so on [5].

Polyvinyl alcohol (PVA), an important polymer, is available in the forms of powders, fibers and films. It is a water-soluble polymer used widely as paper coating agents, adhesives and films. PVA has been used in adhesives for automotive safety glass in textile size and finishes in paper size and coating, as binder for ceramics foundry cases, nonwoven fabric and various pigments [6–13]. Also, PVA acts as an electron donor in the photo reduction process [14]. In this work, 4-mm thick sheet samples from water solution of different PVA concentrations (2 g, 4 g, 5 g and 6 g) were prepared, and it was found that 2 and 4 g PVA sheets were better. In further consequence, the samples were exposed for 15, 30 or 60 min to N$^+$ ion or electron beams produced from a modified saddle field source. The irradiated samples were characterized by UV-Vis spectroscopy to obtain the band gap energy and number of carbon atoms per conjugation length in PVA film, and by scanning electron microscopy (SEM) to check surface morphology and optical properties.

II. METHODOLOGY

Different concentrations of polyvinyl alcohol (2 g, 4 g, 5 g and 6 g) were dissolved in 100 mL distilled water, kept at 70 °C for 6 h for complete dissolution, cast on a glass plate and left to dry for 3 days. Several trials were performed from 2–6 g to obtain smooth, uniform and homogenous surfaces, and the sheet sample prepared from 2 g and 4 g PVA solution had smooth, uniform and homogenous surfaces. The sample sheets were irradiated for 15 min, 30 min and 60 min on a low energy dual ion/electron beam source using nitrogen gas.

TABLE 1. Results of molecular calculation for PVA

Energies (eV)	Values
E_{HOMO}	-10.071
E_{LUMO}	2.456
$\Delta E = E_{HOMO} - E_{LUMO}$	-12.527
Hardness$(\eta) = \Delta E/2$	6.264
Ionization Energy (IE) $= -E_{HOMO}$	10.071
Electron Affinity (EA) $= -E_{LUMO}$	-2.456
Total Energy	-1367.53247

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MO calculations were performed using semi-empirical molecular orbital calculation. The method used in these computations is the parametric method (PM7) described in Refs. [15, 16]. Semi empirical PM7 calculations have been the best in predicting geometric properties and vibrational frequencies of transition and organ metallic metal complexes [17]. The modeling program is run on microcomputer under the molecular orbital calculation package MOPAC2012. The molecular orbital calculations (MOC) was performed using semi-empirical molecular orbital calculation (Table 1). The method used is the parametric method (PM7) described in Ref. [18]. Figure 1 shows geometrical structure of PVA and its numbering system.
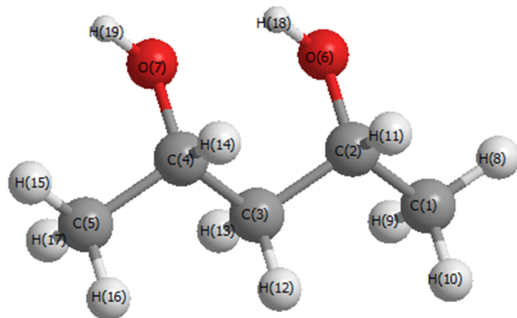

Fig. 1. (Color online) The geometrical structure of PVA ($C_5H_{12}O_2$, Mol. Wt. 104.15).

A. Experimental details

The experimental set-up utilized for ion/electron beam treatment is a home-built system shown in Fig. 2 [19]. It consists of two copper anode rods surrounded by a cylindrical cathode. Placed inside the cylindrical cathode is a Perspex cylinder having two opposite holes of $\Phi 5$ mm for producing ion/electron beam current. PVA samples were put on Faraday cup at distance 1 cm from the cylindrical cathode.
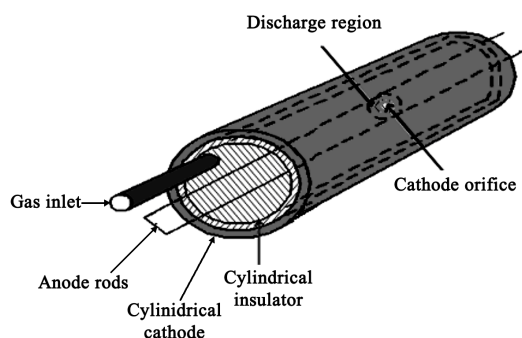

Fig. 2. Schematics of the double beam source.

B. Irradiation of the PVA films

The film samples were irradiated in a vacuum chamber of 10^{-5} mbar. The ion fluence (Φ, in ions/cm^2) was estimated by $\Phi = It/(qeA)$ [3, 20], where I is the ion beam current (A), t is the irradiation time (s), q is charge state of the ion ($q = 1$, in the present study), e is the electron charge (1.6×10^{-19} C), and A is the beam spot area (cm^2).

III. RESULTS AND DISCUSSION

In this study, the system was evacuated to about 3×10^{-5} mbar to remove the residual gases before the nitrogen gas injection. The source apparatus had been polished, and washed by acetone. Polishing the electrodes should remove irregular parts from their surfaces, and the contamination due to the erode materials of the discharge.

A. Operating characteristics of the dual beam source

Nitrogen ion and electron beams from the modified saddle field source were used to irradiate the PVA films. As shown in Table 2, the PVA samples were irradiated by N$^+$ ions or electrons for 15 min, 30 min or 60 min, at N$^+$ ion fluence of 2.81×10^{17}–1.12×10^{18} ion/cm^2, and the electron fluence of 4.21×10^{17}–1.68×10^{18} electrons/cm^2.

TABLE 2. Irradiation parameters of PVA samples.

Samples	Beam fluence (10^{17} ions/cm^2)	
	Electron	N$^+$ ion
I (15 min)	4.219	2.813
II(30 min)	8.438	5.625
III(60 min)	16.88	11.25

Operation characteristics of the ion/electron source were studied under different experimental conditions. Figure 3(a) shows the discharge characteristics using nitrogen gas, i.e. the relationships between the discharge voltage and current at different gas pressures. It can be seen that the discharge current increases with the discharge voltage. Such discharge is characterized by abnormal glow [21, 22]. Figure 3(b) shows the ion beam efficiency, i.e., the relationship between the output ion beam current and the discharge current at different pressures of nitrogen gases. One sees that the ion beam current increases with the discharge current, and reaches its maximum value at N$_2$ pressure of 1.3×10^{-3} mbar [21]. The investigation of electron beam characteristics under different experimental conditions will be published elsewhere [23].

B. Optical investigations

The pristine and irradiated PVA samples were characterized by UV-Vis spectrophotometer in the wavelength of 100–1000 nm at room temperature. Figure 4(a) shows UV-Vis
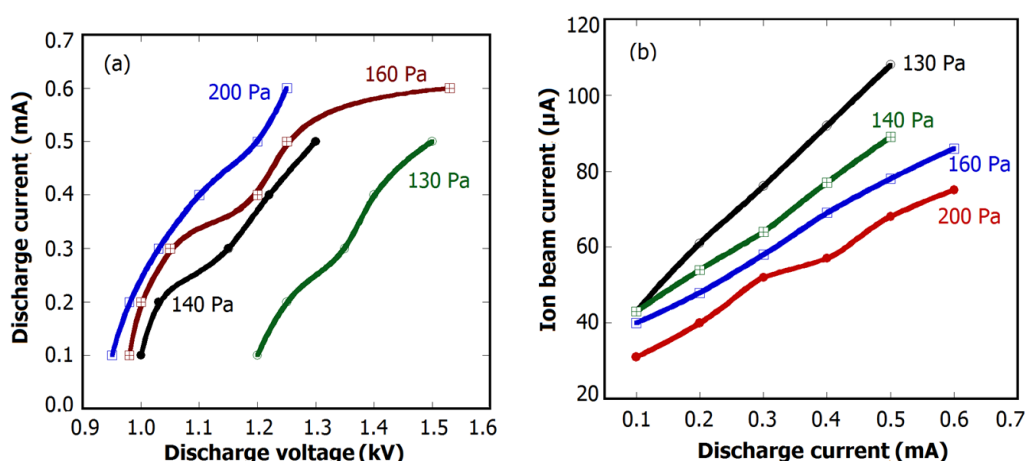
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Fig. 3. (Color online) Relationship between the discharge and output ion beam current at different N_2 gas pressures.
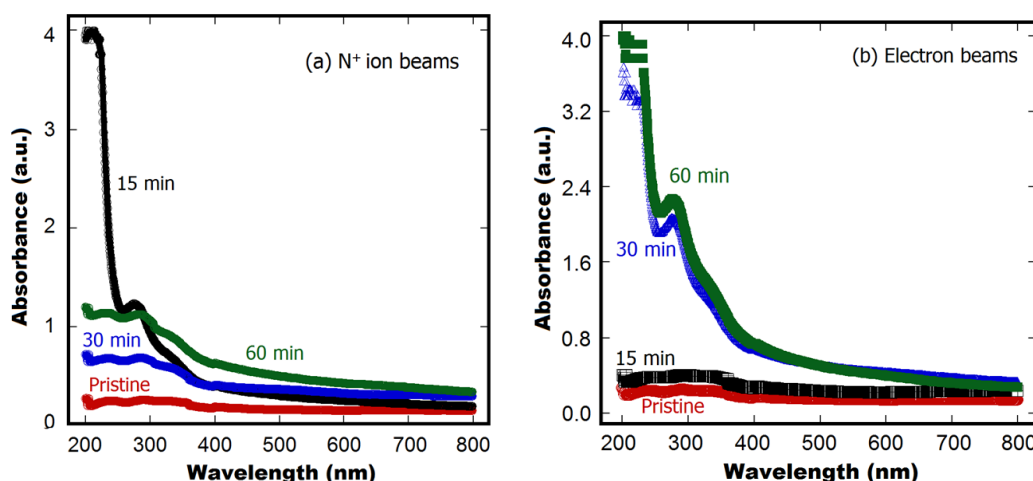

Fig. 4. (Color online) UV-Vis spectra for pure PVA irradiated with (a) N^+ ions beams and (b) electron beams.

spectra of PVA sheets irradiated by N^+ ion beam for 0 min, 15 min, 30 min and 60 min. A shift of absorption edge towards longer wavelength with increasing ions dose can be readily observed. The pristine sample is used as a reference material. UV-vis spectroscopy gives an idea about the value of optical band gap energy (E_g), which is important for materials investigation [24]. The absorption of light by polymeric materials in the ultraviolet and visible regions involves promotions of electrons in σ, π and n-orbitals from the ground state to the higher energy levels [25]. The electronic transitions that are involved in the ultraviolet and visible regions are, σ–σ^*, π–π^* and n–π^* [25]. In Fig. 4(a), two absorbance bands are related to the electronic transitions n–π and π–π^*. The intensity of the two peaks increases with the dose (0, 15, 30 and 60 min). The prominent peaks for ions effect are (201, 288), (206, 275), (205, 283) and (205, 285).

The optical absorption coefficient (α) was calculated using Eq. (1) [26]:

$$\alpha(\nu) = 2.303[\log(I_0/I)]/l, \qquad (1)$$

where l is the sample thickness in cm, and $\log(I_0/I)$ is the absorbance with I_0 and I being intensity of the incident and transmitted beams, respectively. The absorption coefficient near the band edge for non-crystalline materials shows an exponential dependence on the photon energy ($h\nu$) which follows the Urbach formula [27]:

$$\alpha(\nu) = \alpha_0 \exp(h\nu/E_u), \qquad (2)$$

where α_0 is a constant, E_u is the Urbach energy which is interpreted as width of the tail of localized states in the forbidden band gap, ν is the frequency of radiation and h is Planck constant. The E_u values were calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy region of these curves.

Figure 4(b) shows the UV-Vis spectra for PVA sheets irradiated by electron beam for 0, 15, 30 and 60 min. The same behavior as Fig. 4(a) can be seen. The two absorbance bands are related to the electronic transitions n–π and π–π^*. The intensity of the two peaks increases with the electron dose.

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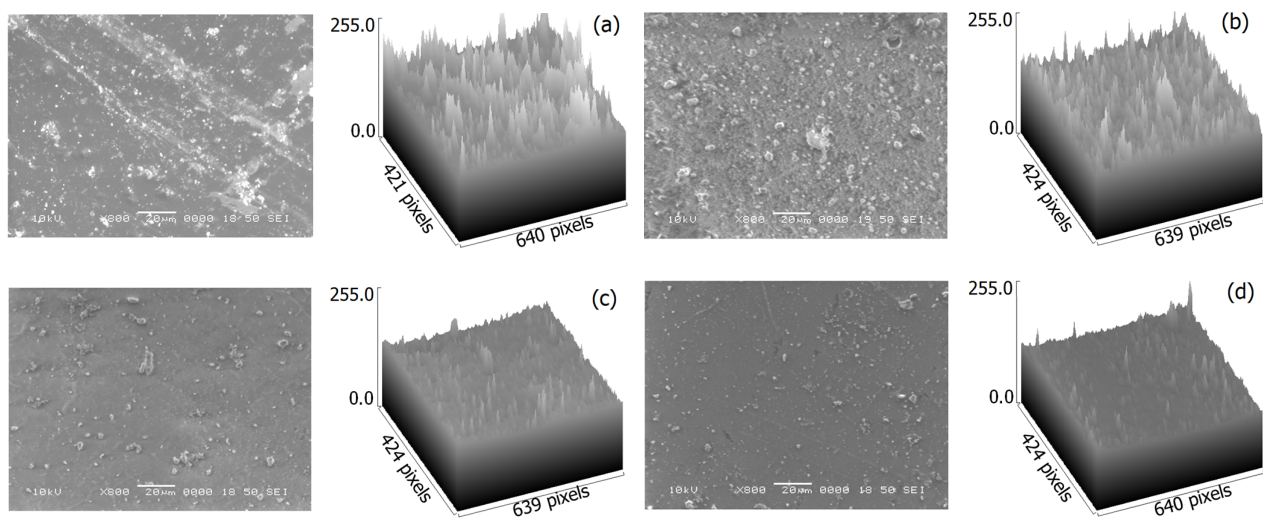Nucl. Sci. Tech. **26**, 060306 (2015)

Fig. 5. SEM images of PVA sheet samples irradiated by N$^+$ ion beams for (a) 0, (b) 15 min, (c) 30 min and (d) 60 min.

The two prominent peaks are related to criteria of the pure PVA irradiated by E-beams for 15, 30 and 60 min. The peaks for electrons effect are (205, 290), (206, 291) and (206, 275). Figure 4(b) shows a large shift with increasing electron doses, which means a huge destructive effect that leads to the formation of more radicals and free electrons, hence the increase in UV-Vis spectra.

Tauc's plot [28] is the usual method for determination of the optical band gap (E_g) from UV-Vis spectrum by fitting the linear part of Tauc's plots, $(\alpha h\nu)^{1/n}$ against $(h\nu)$, where α is the absorption coefficient, h is the Planck constant and ν is the frequency of the incident UV-Vis radiation. Also $n = 1/2$, for direct electronic transition and $n = 2$ for indirect electronic transition [29]. The obtained band gaps are summarized in Table 2. The band gap of N$^+$ ion-irradiated PVA decreases with increasing doses, while the band gap of electron-irradiated PVA increases with the dose. The variation in the band gap can be well attributed to the structural deformation phenomena occurring in the polymer [30, 31]. In case of indirect electronic transition, there is a shift in the position of the valence and the conduction bands. Therefore, phonons exist to conserve momentum [32]. The phonon energy is the energy difference between direct and indirect band gaps [33]. The cluster size is correlated to the band gap energy and could be estimated from [34]: $E_g = 34.3N^{1/2}$, where N is the number of carbon atoms per conjugation length. The calculated clusters sizes for PVA samples are given in Table 3.

Band gap energy decreases with increasing ion dose, while it increases with electron dose. This is due to that ions have greater degradation effect than electrons. Ion /electron beam irradiation of polymers generate a number of charged species such as free radicals, ions and other low molecular weight charged species, and the mobility of these species contribute to the surface conductivity. The decrease in E_g of the N$^+$ ion-irradiated PVA is attributed to a decrease in the mobility

TABLE 3. Optical parameters of PVA films before and after ion/electron irradiation

Samples	E_g (eV)		N	
	Direct	Indirect	Direct	Indirect
Pristine	2.69	2.78	163	152
15 min EB	2.88	2.63	142	170
30 min EB	4.72	4.02	53	73
60 min EB	4.99	4.39	47	61
15 min N$^+$	5.18	4.64	44	55
30 min N$^+$	2.96	2.70	134	161
60 min N$^+$	2.82	2.35	148	213

of the molecular charged species, compared with band gap energy of the electron-irradiated PVA.

C. Surface morphology analysis

SEM images were taken to visualize the changes in surface of the PVA samples irradiated by N$^+$ ion beams 15 min, 30 min and 60 min [35] (Fig. 5). The surface plot tool of Image J software was used to treat first SEM image for the pristine PVA, and then the N$^+$ ion-irradiated PVA samples. N$^+$ ion beam effect can be seen clearly. Of all the N$^+$ ion-irradiated PVA samples, surface morphology of the 30-min irradiation (Fig. 5(c)) appears the most homogenous and rough, being the best eligible surface to be as substrate of another applications (coating and thin film deposition), because surface roughness means that it is more adhesive with added materials.

Figure 6 shows SEM images of the PVA samples irradiated by E-beam for 15 min, 30 min and 60 min. After 15-min E-beam irradiation, the surface was found to be deformed (bubbles); after 30 min treatment, it was less deformation (bubbles disappear); and after 60 min treatment, the surface deformation appears again (without bubbles) and the surface is becoming highly deformed and inhomogeneous.
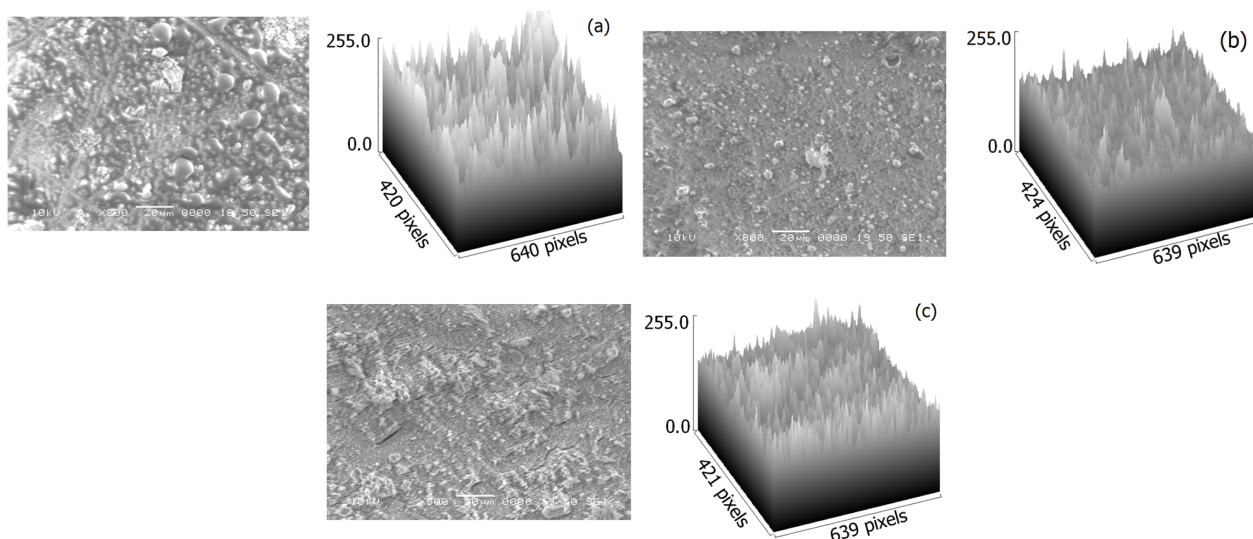
Fig. 6. SEM images of PVA sheet samples irradiated by electron beams for (a) 15, (b) 30 min and (c) 60 min.

The SEM images reveal significant differences before and after ion electron beam treatment, indicating that there was roughness occurred to the PVA polymer surface after ions or electrons treatment.

IV.   CONCLUSION

A modified saddle field ion/electron source was used to modify the surface of PVA substrate for coating or thin film deposition. Nitrogen ion and electron beams were used. SEM images reveal significant differences before and after ion/electron beam treatment, and the 30 min N^+ ion treatment is the best in surface homogeneity and roughness. UV-VIS spectra show small change on energy gap and the change in electric properties is small, too. The induced defects on the polymer surface generate carbon clusters over the surface which improves surface conductivity with the decrease of the band gap with ion irradiation. Finally, low energy nitrogen ion/electron beam from a dual source is a good tool (compared with large ion/electron accelerator machines) to improve surface morphology and enhance the photo-responsive properties of the treated samples.

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